

FLAME RETARDANT POLYOLEFIN BLENDS**Field of Invention:**

The present invention relates to a flame retardant polyolefin blend and a process for the preparation thereof. The blends of this invention neither drip nor glow when ignited and pass UL94 V- 0 test with low emission of nontoxic fumes.

Background of the Invention:

The concept of fire-retardancy is remarkably old. Herodotus, the Greek Historian, in 484-431 BC recorded that the Egyptians imparted fire-resistance to wood by soaking it in a solution of alum (potassium aluminum sulfate). Vitruvius in the 1st Century BC described some military applications of fire retardant materials such as plaster of clay reinforced with hair. Wild was issued a British patent in 1735 for his process of treating wood with a mixture of alum, ferrous sulfate and borax (sodium tetra borate decahydrate). And Gay-Lussac in 1821 showed that a solution of ammonium phosphate, ammonium chloride and borax acts as a fire retardant for wood.

In all these processes the key ingredients are the elements from Group III (B and Al) of the periodic table. Even at the beginning of the 21st Century, with so much of research activity for better fire retardants, the most effective elements are still found in Group: III (B and Al), V (N₂, P and Sb) and VII (Cl and Br). Research efforts are on to find new and improved flame retardant (FR) agents for synthetic and natural polymers. Certain compounds such as melamine (2,4,5-triamino- 1,3,5-triazine) and its derivatives are also found to be effective flame-retardants, because of their ability to employ various modes of flame retardant action. The growing interest for melamine based flame retardants is further more driven by the particular advantages these products offer over existing flame retardants: cost effective, low smoke density and toxicity, low corrosion and safe handling. In the present process, melamine and/or its derivatives when used in conjunction with an inorganic hydroxide was found to impart flame retardancy to the polyolefins. Inorganic non-halogen FR compounds such as zinc borate; ammonium phosphate and organic phosphorous-based chemicals are also being used for providing flame resistivity to polymers.

Several attempts have been made for developing fire retardant polyolefins. US Patent 3,936,416 (1976) issued to Brady described a process for preparing no burning, no dripping, char-forming polypropylene composition with melamine pyrophosphate dipentacrythritol and other systems. US Patent 4,010,137 (1977) granted to Brady again

illustrates phosphorus containing flame retardant along with melamine for synthetic resins. US Patent 5,124,404 (1992) granted to Atwell, Ray W., *et al.*, of Great Lakes Chemical Corp. describes flame-retardant polypropylene (with grafted side chain having brominated monomer units) molding compositions, which exhibit good physical properties in combination with flame retardancy. Imahasi *et al.*, (1996) described in their US Patent No.5,583,172 flame-retardant composition in which aluminum or magnesium hydroxide was used to impart color stability against heat. Chapline *et al.*(1994) in their US Patent No. 5,342,874 described flame retardant polymer formulation in which synergistic mix of flame-retardants such as aluminum or magnesium hydroxide of trioxide etc. were used. A novel magnesium hydroxide as fire-retardant for thermoplastic synthetic resins and aqueous paints was disclosed by Miyata *et al.* (1979) in their US Patent No. 4,145,404. US Patent No. 6,414,070 (2002) issued to Charles Kausch, *et al.*, of Omnova Solution Inc., presents flame-resistant nanocomposite polyolefin composition containing organically modified clays. In all these above inventions the use of melamine or its derivatives in conjunction with a metal hydroxide as flame-retardant for polyolefins was not reported. The synergistic effect of such combination in the presence of certain other chemicals is described here.

Objects of the Invention

It is an object of the invention to obtain polyolefin blends with melamine and other additives that allow injection molding, compression molding, thermoforming and other conventional techniques to be applied for making end-products such as, electrical meter housings, various furniture/general items that can be used in cars, buses, railway coaches and other motorized vehicles.

It is another object of the invention to develop a process for the preparation of flame retarded polyolefin blends with melamine and other additives that provide a synergistic effect in flame retardancy along with balanced mechanical properties, using a twin- screw extruder or a Buss co-kneader.

Summary of the Invention

The present invention provides a fire-resistant polyolefin blend comprising a polyolefin and melamine or it's derivative along with a melt flow improver and having melt flow index in the range: 2 – 15g/10 min. when tested according to ASTM D1238.

In an embodiment, the base polymer of the polyolefin blend is a homopolymer of propylene or ethylene, or a block or a random copolymer of ethylene and propylene and is present in a concentration range of from 30 to 88 wt.%.

In an embodiment, the blend comprises of (i) a polyolefin base polymer (ii) melamine or its derivative (iii) a flame retardant and (iv) a compatibilizer.

In a preferred embodiment, the polyolefin base polymer is selected from an isotactic or syndiotactic polypropylene homopolymer or a blend of the two; said melamine derivative is selected from melamine cyanurate or melamine phosphate; said flame retardant is selected from magnesium hydroxide and/or aluminum trihydroxide, zinc borate and ammonium phosphate and said compatibilizer comprises a maleic anhydride grafted polypropylene (MAH-g-PP) or a suitable organo silane.

In an embodiment, said polyolefin polymer has a melt flow index in the range of 12 to 40 g/10 min. when tested at 230°C at 2.16 kg load (according to ASTM D1238).

In an embodiment, said melamine or its derivative is present in the concentration range of 10 to 50wt %.

In another preferred embodiment, said flame retardant, preferably an inorganic hydroxide, is present in the concentration range of 2 to 10wt %.

In an embodiment, the blend additionally includes a processing aid such as a fluoroelastomer in the concentration range of 1 to 2wt %.

In an embodiment, the blend additionally includes an antioxidant, preferably trionyl phenylphosphites, in a concentration range of 0-3wt %.

This invention also provides a process for preparation of polypropylene blends with melamine and/or its derivatives along with other ingredients extruded in a twin screw extruder or a Buss co-kneader all together or in separate batches, wherein for example, twin screw extruder temperature is maintained in the range: 180 – 250°C and the screws are rotated at a speed of: 50 – 100 rpm.

In another embodiment of the invention, the FR blends qualify the flame retardancy test, UL94 V-0.

Detailed Description of the Invention

This invention is carried out with a polyolefin polymer, received in the form of granules/spheri-beads, after adequately adding the stabilizers and anti-oxidants after polymerization in the plant. The term polyolefin is used to refer to polypropylene

homopolymer, polyethylene (such as low density polyethylene, LDPE, high density polyethylene, HDPE) and reactor copolymers (both random and block copolymers) of propylene and ethylene.

5 The copolymer granules are dehumidified at 80 (+/-) 5°C for two hours, in an oven, preferably, with an air circulation facility.

Melamine or one of its derivatives (melamine cyanurate or melamine polyphosphate) was also dried separately in an oven at a preferred temperature 80 (+/-) 5°C for a period of at least two hours. Similarly, metal hydroxide was also pre-dried at the same above-mentioned conditions.

10 The objective of melt blending is to uniformly disperse melamine or melamine derivative and other additives throughout the polymer matrix. This is achieved by means of a twin-screw extruder, or a Buss co-kneader with a specially designed screw profile that facilitates intimate mixing of the ingredients.

Dried polyolefin (PO) granules, melamine/melamine derivative, metal
15 hydroxide, fluoroelastomer and a compatibilizer were tumble-mixed along with other ingredients in the composition given here: PO: 30-88 wt%; melamine/melamine derivative: 10-50wt %; metal hydroxide: 2-10 wt%; maleic anhydride – grafted – polypropylene (MAH-g-PP) or an organo silane compatibilizer: 0-10wt% all together 100% by weight, and in addition other additives viz. glycerinemono-stearate, calcium
20 stearate, Tinuvin-770, Tinuvin-327, Blend- 225 and Chimmasorb, a combination of Tinuvin 622 and Benzophenone 0.01 – 0.1 phr. each. A Buss co-kneader or a co-rotating twin screw extruder with a preferred screw profile that would enhance intimate mixing of ingredients was used under the following conditions: temperature range: 180–250 °C, screw speed: 50-100 rpm, residence time: 2-5 min. The extrudates were
25 dipped in circulating cold water and later chopped into granules of length 2-4 mm.

The extrudates granules were dried and were injection molded into ASTM standard test specimens for evaluating various performance properties such as burning test, tensile, flexural, Izod impact, heat deflection temperature etc. The dried granules were also used to measure melt flow index, thermal stability (using thermo gravimetric
30 analyzer).

Computer controlled injection molding machine was used with temperature profile (with four heating zones) in the temperature range: 180 – 230°C, injection pressure (applied in six stages): 15-125 kg/cm², injection time (in six stage): 2.5 – 5.0

sec., with screw speed (in two stages) in the range: 80-100 rpm. Standard test specimens, thus obtained, were used for evaluating various performance properties of the compounds following the ASTM standard test methods.

Melamine based flame retardants are growing in their popularity as end-use customers discover their virtues, which includes low smoke and toxic gas evolution in fire situations, low corrosion to metals such as those used in extruders and molding machines and low corrosion to metal contacts or wires in electrical and electronic applications. These virtues of melamine-based flame-retardants are inherent in their flame retarding mechanism: multiple actions such as endothermic decomposition and reactions in the solid and gas phases in fire situations. These nitrogen based environment friendly flame-retardants also offer a way to reuse/recycle the polyolefin blends.

The present invention will now be illustrated with reference to the following non-restrictive Examples.

Example – 1:

Dried granules of polypropylene homopolymer (50-75 wt %) were mixed with dry melamine or melamine based compound, in the concentration range: 20-40 wt % and metal hydroxide in the concentration range: 2-10 wt% in a high-speed sigma-mixer. The dry mixture was extruded in a Buss co-kneader with a preferred screw profile. The extrusion was carried out with the extruder operating in the temperature range: 150 –215°C with screw rotating at 60 rpm. The extrudate strands (say Blend-A) were dipped in a trough of water that was circulated in order to keep them cool. Then the strands were dried and granulated.

The dry granules of Blend-A were injection molded to get ASTM standard test specimens using FRK-85, Klockner-Windsor injection molding machine under the molding conditions given below in Table –I.

Table –I

Typical injection molding condition for preparing ASTM test specimens

No.	Processing Parameter	Units	Typical Value
1.	Injection pressure	kg/cm ²	70-120
2.	Temperature maintained	°C	150-230

3.	Injection time	sec.	3-10
4.	Cooling time	sec.	25-100
5.	Screw speed	rpm.	70-100

The properties of the blends injection molded under the above conditions are given in Table -II.

Table -II

Typical properties of Blend-A

No.	Property	ASTM method	Unit	Blend-A
1.	Melt flow index	D1238	h/10min.	1.5
10 2.	Tensile strength	D638	kg/cm ²	173
3.	Tensile modulus	D638	kg/cm ²	-
4.	Flexural strength	D790	kg/cm ²	318
5.	Flexural modulus	D790	kg/cm ²	-
15 6.	Notched Izod impact strength 3.2mm thick specimens*	D256	kg.cm/cm	1.88
	6.4mm thick specimens			
7.	Heat deflection temperature			
	At 4.6 kgf stress	D648	°C	120
20	At 18.2 kgf stress			
8.	Flammability	UL94	--	V-0

(*Middle portions of the injection molded ASTM standard tensile specimens were used)

Example-2

Pre-dried granules of copolymer of propylene and ethylene (PPCP) (50-80 wt%), melamine/ melamine derivative (20-45 wt%) and Aluminum tri-hydroxide (0-5 wt%) were mixed in a high-speed sigma mixer along with other additives viz. processing aid and antioxidants. The entire dry blended mixture was melt extruded in a Buss co-kneader as described in Example-1, using similar extrusion conditions and the granules of this blend (say Blend-B) were later injection molded on a Klockner-Windsor machine (FRK-85), under identical conditions described previously.

The injection molded ASTM test specimens were used to evaluate the performance properties of the Blend-B given in Table-III.

Table –III.
Typical properties of Blend-B

No.	Property	ASTM method	Unit	Blend-B
5	1. Melt flow index	D1238	g/10min.	9.92
	2. Tensile strength (at break)	D638	kg/cm ²	180
	3. Flexural modulus	D790	kg/cm ²	24,250
	4. Notched Izod impact strength 6.4mm thick specimens.	D256	kg.cm/cm	3.22
10	Heat deflection temperature At 4.6 kgf stress	D648	°C	110.5
	At 18.2 kgf stress			
	6. Flammability	UL94	--	V-0.

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Example-3.

Dried granules of PPCP (50-70wt.%) were mixed with dried melamine (20-40 wt.%) and Aluminum tri hydrate (5-10 wt.%). To this mixture was added MAH-g-PP (2-5 wt.%), processing aid, antioxidants and other additives mentioned above. The ingredients were mixed thoroughly in a high speed Sigma mixer and extruded in a similar fashion as described in Example-1, on a Buss co-kneader. The extrudate strands (say Blend-C) was granulated following the same procedure as in the previous experiment. ASTM standard test specimens were prepared using the same injection-molding machine under identical conditions described earlier.

25 The typical properties of Blend-C are given in Table-IV.

Table –IV.
Typical properties of Blend-C

No.	Property	ASTM method	Unit	Blend-C
30	1. Melt flow index	D1238	g/10min.	7.56
	2. Tensile strength(at break)	D638	kg/cm ²	170.6
	3. Flexural modulus	D790	kg/cm ²	19,770

4.	Notched Izod impact strength 3.2mm thick specimens. *	D256	kg.cm/cm	3.3
5.	Heat deflection temperature			
5	At 4.6 kgf stress	D648	°C	---
	At 18.2 kgf stress			
6.	Flammability	UL94	—	V-0.
10	(*Middle portions of the injection molded ASTM standard tensile specimens were used)			

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